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(54)   Composition for preparing porous dielectric thin film containing saccharides porogen

(57)   The present invention provides a composition for preparing porous interlayer dielectric thin film, said composition comprising a saccharide or saccharide derivative, a thermo-stable organic or inorganic matrix precursor, and a solvent for dissolving said two solid components. There is also provided a dielectric thin film having evenly distributed nano-pores with a diameter less than 50Å, which is required for semiconductor devices.

EP 1 416 501 A2

Description

[0001] The present invention relates to a composition for preparing porous interlayer dielectric thin film containing saccharides porogen. More specifically, the present invention relates to a composition comprising saccharide derivatives as porogen, capable of forming nano-pores with a diameter less than 50Å and a process for preparing porous semiconductor interlayer dielectric thin film in semiconductor device.

[0002] Substances having nano-pores have been known to be useful for absorbents, carriers for catalysts, thermal insulators and electric insulators in various fields. In particular, they have been recently reported useful as materials for insulating films between interconnect layers in semiconductor devices. As the integration level has been increased in semiconductor devices, the performance of the devices is determined by the speed of wires. Accordingly, the storage capacity of interconnect thin film is required to be lowered to decrease the resistance and capacity in wires. For this purpose, there have been attempts to use materials with low dielectric constant in the insulating film. For example, US Patent Nos. 3,615,272, 4,399,266 and 4,999,397 disclose polysilsesquioxanes with a dielectric constant of 2.5~3.1 which can be used in Spin On Deposition(SOD), as an alternative for SiO_2 with a dielectric constant of 4.0 which has been used in Chemical Vapor Deposition(CVD). In addition, US Patent No. 5,965,679 describes organic high molecules with a dielectric constant of 2.65~2.70, polyphenylenes. However, the dielectric constants of the previous matrix materials are not sufficiently low to achieve a very low dielectric constant less than 2.50 required for high-speed devices.

[0003] To solve this problem, there have been various trials to incorporate air bubbles into these organic and inorganic matrixes at a nano-scale. In this connection, US Patent No. 6,231,989 B1 describes a method to form a porous thin film by the treat of the ammonia through the mixing of high boiling point solvent, which can form pores on the hydrogen silsesquioxane. Further, US Patent Nos. 6,114,458, 6,107,357 and 6,093,636 disclose a method for preparing very low dielectric constant substances comprising the steps of: vinyl-based high molecular dendrimer porogen which is degradable in the heating step in the same method with that disclosed in US Patent No.6,114,458; and mixing the dendrimer porogen with organic or inorganic matrix; making a thin film using the mixture; and decomposing the porogens contained in the mixture at a high temperature to form nano-pores. However, the porous substances produced by such methods have a problem that their pore sizes are as large as 50~100Å in diameter and distribution thereof is ununiform.

[0004] A feature of the present invention is to provide a composition for preparing dielectric thin film wherein a number of pores with a diameter less than 50Å are uniformly distributed.

[0005] Another feature of the present invention is to provide a method for forming dielectric thin film between interconnect layers in semiconductor devices, which have a dielectric constant k of 2.5 or less, by using said composition.

[0006] In accordance with one aspect of the present invention, there is provided a composition for preparing substances having porous interlayer dielectric thin film, said composition comprising a saccharide or saccharide derivative; a thermo-stable organic or inorganic matrix precursor; and a solvent for dissolving both the saccharide or saccharide derivative and the matrix precursor.

[0007] In accordance with another aspect of the present invention, there is provided a method for forming dielectric thin films between interconnect layers in semiconductor devices, said method comprising: coating a composition comprising a saccharide or saccharide derivative, a thermo-stable organic or inorganic matrix precursor, and a solvent for dissolving both the saccharide or saccharide derivative and the matrix precursor on a substrate through spin-coating, dip-coating, spray-coating, flow-coating, or screen-printing; evaporating the solvent therefrom; and heating the coating film at 150~600°C under inert gas atmosphere or vacuum condition.

[0008] In accordance with still another aspect of the present invention, there is provided a substance having nano-pores, said substance being prepared by using the composition comprising a saccharide or saccharide derivative, a thermo-stable organic or inorganic matrix precursor, and a solvent for dissolving both the saccharide or saccharide derivative and the matrix precursor.

[0009] The above and other features and advantages of the present invention will become more apparent after reading the following detailed description when taken in conjunction with the drawing in which:

Fig. 1 is a graph showing a pore size distribution of thin film prepared in Example 6-3.

Fig. 2 is a graph showing a pore size distribution of thin film prepared in Example 6-4.

[0010] Hereinafter, the present invention will be explained in more detail in the following Examples with reference to the accompanying drawings.

[0011] According to the present invention, there is provided novel substances having evenly distributed nano-pores with a diameter less than 50Å, wherein said substances are made from a composition comprising thermo-stable organic or inorganic matrix precursors and thermo-unstable saccharide derivatives. These substances can be applied to a range of uses, including absorbent, carriers for catalysts, thermal insulators, electric insulators, and low dielectrics. In particular, these substances can be used to form thin films having very low dielectric constant as insulating films between interconnect layers in semiconductor devices.

[0012] The thermo-stable matrix precursors used in the composition of the present invention may be organic or inorganic high molecules having a glass transition temperature higher than 400°C.

[0013] Examples of these inorganic high molecule include, without limitation, (1)silsesquioxane, (2)alkoxy silane sol with a number average molecular weight of 500~20,000 derived from partial condensation of $SiOR_4$, $RSiOR_3$ or R_2SiOR_2 (R is organic substituents), (3) a polysiloxane with a number average molecular weight of 1000~1000,000 derived from partial condensation of more than one kind of cyclic or cage structure-siloxane monomer selectively mixing with more than one kind of silane based-monomer such as $Si(OR)_4$, $Rsi(OR)_3$ or $R_2Si(OR)_2$(R is organic substituents).

[0014] Particularly, the silsesquioxane can be exemplified by hydrogen silsesquioxane, alkyl silsesquioxane, aryl silsesquioxane, and copolymer of these silsesquioxanes.

[0015] In addition, organic high molecules, which cure into stable reticular structure at a high temperature, are also preferred as the matrix precursor. Non-limiting examples of the organic high molecule include polyimide-based polymers, which can be imidized, such as poly (amic acid), poly (amic acid ester), etc.; polybenzocyclobutene-based polymers; and polyarylene-based polymers such as polyphenylene, poly (arylene ether), etc.

[0016] In the present invention, the matrix precursor is more preferably an organic polysiloxane, having Si-OH content of at least 10mol%, preferably 25mol% or more, which is prepared through hydrolysis and polycondensation of at least one siloxane monomer having cyclic or cage structure by using acidic catalyst and water in the presence of a solvent, selectively mixing with at least one silane monomer such as $Si(OR)_4$, $Rsi(OR)_3$ or $R_2Si(OR)_2$(R is organic substituents). The mole ratio of siloxane monomer having either cyclic or cage structure to the silane monomer is 0.99:0.01 ~ 0.01: 0.99, more preferably 0.8:0.2 ~ 0.1:0.9, preferably 0.6:0.4 ~ 0.2:0.8 range.

[0017] The siloxane monomer having cyclic structure can be represented by the following formula (1):

$$\left[\begin{array}{c} R \\ | \\ -Si- \\ | \\ CH_2(CH_2)_mSiX_1X_2X_3 \end{array} -O- \right]_p$$
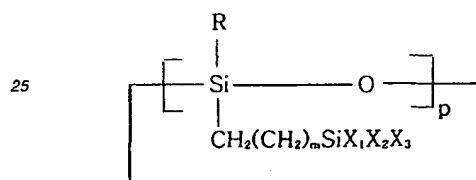
(1)

[0018] In the above formula (1),

R is hydrogen atom, C_{1-3} alkyl group, C_{3-10} cycloalkyl group, or C_{6-15} aryl group;
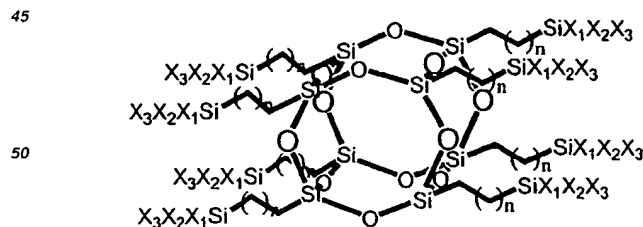
X_1, X_2 and X_3 are independently C_{1-} alkyl group, C_{1-10} alkoxy group, or halogen atom, and at least one of them is a hydrolysable group;

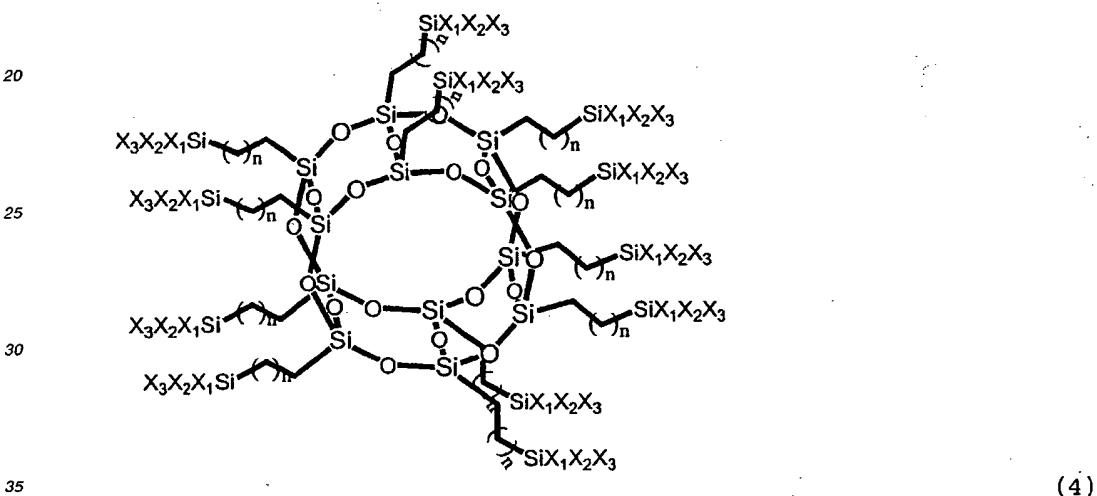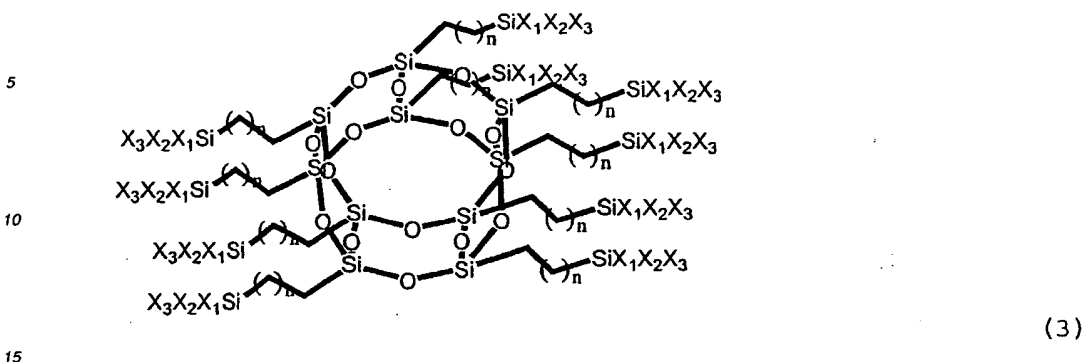p is an integer ranging from 3 to 8; and

m is an integer ranging from 0 to 10.

[0019] The method for preparing the cyclic siloxane monomers is not specifically limited, but hydrosilylation using a metal catalyst is preferred.

[0020] The siloxane monomers having cage structure can be represented by the following formulas (2) to (4):
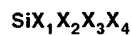

(2)

3

(3)

(4)

[0021]   In the above formulas (2) to (4),

X_1, X_2 and X_3 are independently C_{1-3} alkyl group, C_{1-10} alkoxy group, or halogen atom, and at least one of them is hydrolysable; and
n is an integer ranging from 1 to 12.

[0022]   As can be seen from the above formulas (2) to (4), silicon atoms are linked to each other though oxygen atoms to form cyclic structure, and the end of each branch comprises organic groups constituting a hydrolysable substituent.
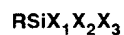
[0023]   The method of preparing siloxane monomers having cage structure is not specially limited, but hydrosilylation using metallic catalyst is preferred.

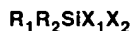[0024]   The silane-based monomers can be represented by the following formulas (5) to (7):

$$SiX_1X_2X_3X_4$$

(5)

$$RSiX_1X_2X_3$$

(6)

$$R_1R_2SiX_1X_2$$

(7)

[0025] In the above formulas (5) to (7),

R$_1$ and R$_2$ are respectively hydrogen atom, C$_{1-3}$ alkyl group, C$_{3-10}$ cycloalkyl group, or C$_{6-15}$ aryl group; and X$_1$, X$_2$, X$_3$ and X$_4$ are independently C$_{1-3}$ alkyl group, C$_{1-10}$ alkoxy group, or halogen atom.

[0026] The catalyst used in the condensation reaction for preparing matrix monomers is not specifically limited, but preferably hydrochloric acid, benzenesulfonic acid, oxalic acid, formic acid, or mixtures thereof.

[0027] In the hydrolysis and polycondensation reaction, water is added at 1.0~100.0 equivalents, preferably 1.0~10.0 equivalents per one equivalent of reactive groups in the monomers, and the catalyst is added at 0.00001~10 equivalents, preferably 0.0001~5 equivalents per one equivalent of reactive groups in the monomers, and then the reaction is carried out at 0~200°C, preferably 50~110°C for 1~100hrs, preferably 5~24hrs. In addition, the organic solvent used in this reaction is preferably aromatic hydrocarbon solvent such as toluene, xylene, mesitylene, acetone, etc.; ketone-based solvent such as methyl isobutyl ketone, acetone, etc.; ether-based solvent such as tetrahydrofuran, isopropyl ether, etc.; acetate-based solvent such as propylene glycol monomethyl ether acetate; amide-based solvent such as dimethylacetamide, dimethylformamide, etc.; γ-butyrolactone; silicon solvent; or a mixture thereof.

[0028] The thermo-unstable porogens used in the present invention are monomeric, dimeric, a polymeric saccharide or a derivative thereof comprising of 1~22 of hexacarbon saccharides.
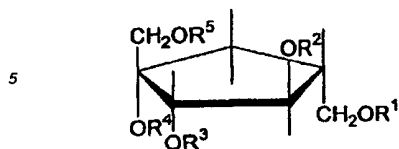
[0029] Concrete examples are monosaccharides such as glucose derivatives represented by the following formula (8), galactose derivatives represented by the following formula (9), fructose derivatives representative by the following formula (10) :
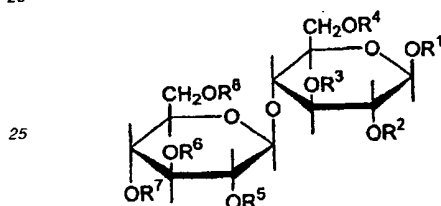

(8)

(9)
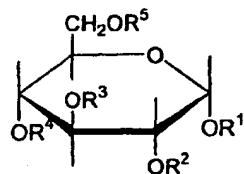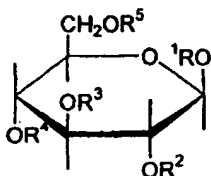
(10)

[0030] In the above formulas (8) to (10),

R_1, R_2, R_3, R_4 and R_5 are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10} cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group, or C_{1-20} carboxyl group.
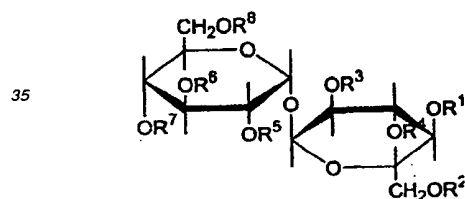
[0031] Another examples of the porogen used in the present invention is disaccharides such as lactose derivatives represented by the following formula (11), maltose derivatives represented by the following formula (12), disaccharide-based sucrose derivatives represented by the following formula (13).

(11)

(12)

(13)
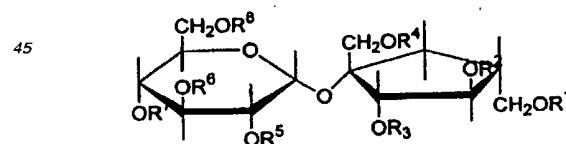
[0032] In the above formulas (11) to (13),

R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10} cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group, C_{1-20} carboxy alkyl group.

[0033] Yet another examples of the porogen used in the present invention is polysaccharide represented by the following formula (14).

(14)
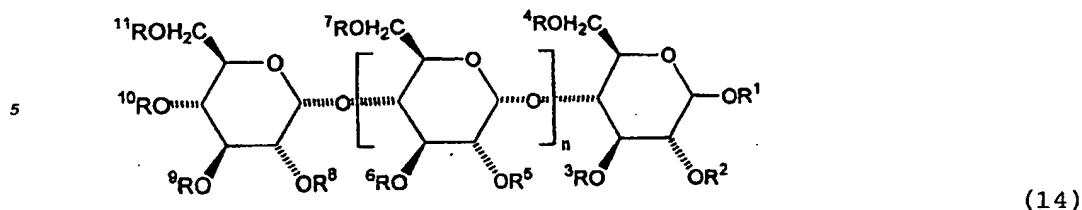
[0034] In the above formula (14),

R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10} cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group, or C_{1-20} carboxyl group and n is an integer ranging from 1 to 20.

[0035] Specific examples of the porogen include, but not limited to, glucose, glucopyranose pentabenzoate, glucose pentaacetate, galactose, galactose pentaacetate, fructose, sucrose, sucrose octabenzoate, sucrose octaacetate, maltose, lactose, etc.

[0036] The content of the saccharide is preferably 0.1~95 wt.%, more preferably 10~70 wt.% of the solid components (matrix precursor + porogen). If the porogen is used more than 70 wt.% there is a problem that a thin film is not used interlayer insulator because the mechanical property of the film is lowered. To the contrary, if the porogen is used less than 10wt.%, the dielectric constant of the film is not lowered due to the lowered generation of pores.

[0037] In the present invention, the composition for producing substances having nano-pores may be prepared by dissolving the above mentioned thermo-stable matrix precursors and a saccharide or saccharide derivative in an appropriate solvent. Examples of this solvent include, but not limited to, aromatic hydrocarbons such as anisole, mesitylene and xylene; ketones such as methyl isobutyl ketone, 1-methyl-2-pyrrolidinone and acetone; ethers such as tetrahydrofuran and isopropyl ether; acetates such as ethyl acetate, butyl acetate and propylene glycol methyl ether acetate; amides such as dimethylacetamide and dimethylformamide; γ-butyolactone; silicon solvents; and mixtures thereof.

[0038] The solvent should be used in sufficient amount to coat a substrate fully with the two solid components (matrix precursor + a saccharide or saccharide derivative), and may be present in the range of 20~99.9 wt.% in the composition, preferably 50~95 wt.%. If the solvent is used less than 20 wt.%, there is a problem that a thin film is not formed evenly due to high viscosity. To the contrary, if the solvent is used more than 99.9 wt.%, the thickness of the film is too thin.

[0039] According to the present invention, the thin film having nano-pores is formed on a substrate by the use of the composition of the present invention, and serves as a good interlayer insulating film required for semiconductor devices. The composition of the present invention is first coated onto a substrate through spin-coating, dip-coating, spray-coating, flow-coating, screen-printing and so on. More preferably, the coating step is carried out by spin-coating at 1000-5000 rpm. Following the coating, the solvent is evaporated from the substrate for a resinous film to deposit on the substrate. At this time, the evaporation may be carried out by simple air-drying, or by subjecting the substrate, at the beginning of curing step, to vacuum condition or mild heating (≤100°C). The resulting resinous coating film may be cured by heating at a temperature of 150~600°C, more preferably 200~450°C wherein pyrolysis of the saccharide porogen occurs, so as to provide insoluble film without crack. As used herein, by "film without crack" is meant a film without any crack observed with an optical microscope at a magnification of 1000X. As used herein, by "insoluble film" is meant a film, which is substantially insoluble in any solvent described as being useful for the coating and deposition of the siloxane-based resin. The heat-curing of the coating film may be performed under inert gas (nitrogen, argon, etc.) atmosphere or vacuum condition for even 10 hrs, preferably 30 min to 2 hrs.

[0040] After the curing, fine pores with a diameter less than 50Å is formed in the matrix. More fine pores with a diameter less than 30Å may be evenly formed, for example, through chemical modification of saccharide porogen.

[0041] The thin film obtained from the above has a low dielectric constant (k≤2.5). Further, in the case that 30 weight parts of the saccharide porogen are mixed with 70 weight parts of the matrix precursor (i.e.; content of the saccharide is 30wt.% of the solid mixture), very low dielectric constant (k≤2.2) may be also achieved.

[0042] Hereinafter, the present invention will be described in more detail with reference to the following Examples. However, these Examples are given for the purpose of illustration and are not to be construed as limiting the scope of the invention.

Example 1 - Synthesis of matrix monomers

Example 1-1: Synthesis of matrix monomer A

[0043] To a flask were added 29.014mmol (10.0g) of 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane and 0.164g of platinum (O)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex(solution in xylene), and then diluted with 300ml diethylether. Next, the flask was cooled to -78°C, 127.66mmol(17.29g) trichlorosilane was slowly added thereto, and then the flask was slowly warmed to room temperature. The reaction was continued at room temperature for 20hrs, and any volatile materials were removed from the reaction mixture under reduced pressure of about 0.1torr. To the mixture was added 100ml pentane and stirred for 1hr, and then the mixture was filtered through celite to provide a clear colorless solution. The pentane was evaporated from the solution under reduced pressure of about 0.1torr to afford a colorless liquid compound, [-Si(CH$_3$)(CH$_2$CH$_2$SiCl$_3$)O-]$_4$ in a yield of 95%. 11.28mmol (10.0g) of the compound was diluted with 500ml tetrahydrofuran, and 136.71mmol (13.83g) triethylamine was added thereto. Thereafter, the mixture was cooled to -78°C, 136.71mmol (4.38g) methyl alcohol was slowly added thereto, and it was slowly warmed again to room temperature. The reaction was continued at room temperature for 15hrs followed by filtration of the product mixture through celite, and then volatile materials were evaporated from the filtrate under reduced pressure of about 0.1torr. Subsequently, 100ml pentane was added thereto and stirred for 1hr, and then the mixture was filtered through celite to provide a clear colorless solution. The pentane was evaporated from this solution under reduced pressure of about 0,1torr to afford monomer A represented by the following formula (15) as a colorless liquid in a yield of 94%:
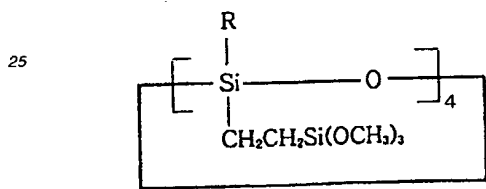
(15)

Example 2 - Synthesis of matrix precursors

Example 2-1 Precursor A : Homopolymerization of monomer A

[0044] To a flask was added 9.85mmol (8.218g) monomer A, and then diluted with 90ml tetrahydrofuran. Next, dil. HCl solution (1.18mmol hydrochloride) prepared by mixing of 8.8ml conc. HCl (35wt.% hydrochloride) with 100ml D. l.-water was slowly added thereto at -78°C, followed by addition of more D.l.-water, so that total amount of water including the inherent water in the above added dil. HCl solution might be 393.61mmol (7.084g). Thereafter, the flask was slowly warmed to 70°C, and allowed to react for 16hrs. Then, the reaction mixture was transferred to a separatory funnel, 90ml diethylether was added thereto, and then rinsed with 100ml D.l.-water 5times. Subsequently, 5g anhydrous sodium sulfate was added thereto and stirred at room temperature for 10hrs to remove a trace of water, and then filtered out to provide a clear colorless solution. Any volatile materials were evaporated from this solution under reduced pressure of about 0.1torr to afford 5.3g of precursor A as white powder.

Example 2-2

Precursor B: Copolymerization of monomer A and methyltrimethoxysilane

[0045] To a flask were added 37.86mmol (5.158g) methyltrimethoxysilane and 3.79mmol (3.162g) monomer A, and then diluted with 100ml tetrahydrofuran. Next, dil. HCl solution (0.0159mmol hydrochloride) prepared by dilution of 0.12ml conc. HCl (35wt.% hydrochloride) with 100ml D.l.-water was slowly added thereto at -78°C, followed by addition of more D.l.-water, so that total amount of water including the inherent water in the above added dil. HCl solution may be 529.67mmol (9.534g). Thereafter, the flask was slowly warmed to 70°C, and allowed to react for 16hrs. Then, the reaction mixture was transferred to a separatory funnel, 100ml diethylether was added thereto, and then rinsed with 100ml D.l.-water five times. Subsequently, 5g anhydrous sodium sulfate was added thereto and stirred at room tem-

perature for 10hrs to remove a trace of water, and then filtered out to provide a clear colorless solution. Any volatile materials were evaporated from this solution under reduced pressure of about 0.1torr to afford 5.5g of precursor B as white powder.

Example 2-3

Precursor C: Copolymerization of monomer A and tetramethoxy silane

[0046] To a flask were added 13.28mmol (11.08g) monomer A and 2.39mmol (2.00g) tetramethoxy silane, and then diluted with 100ml tetrahydrofuran. Next, dil. HCl solution (0.0159mmol hydrochloride) prepared by dilution of 0.12ml conc. HCl (35wt.% hydrochloride) with 100ml D.I.-water was slowly added thereto at -78°C, followed by addition of more D.I.-water, so that total amount of water including the inherent water in the above added dil. HCl solution may be 529.67mmol (9.534g). Thereafter, the flask was warmed to 70° C, and allowed to react for 16hrs. Then, the reaction mixture was transferred to a separatory funnel 100ml diethylether was added thereto, and then rinsed with 100ml D. I.-water five times. Subsequently, 5g of anhydrous sodium sulfate was added thereto and stirred at room temperature for 10hrs to remove a trace of water, and then filtered out to provide a clear colorless solution. Any volatile materials were evaporated from this solution under reduced pressure of about 0.1torr to afford 6.15g of precursor C as white powder.

Example 3: Analysis of the prepared precursors

[0047] The siloxane-based resinous precursors thus prepared were analyzed for weight average molecular weight (hereinafter, referred to as "MW") and molecular weight distribution (hereinafter, referred to as "MWD") by means of gel permeation chromatography (Waters Co.), and the Si-OH, Si-OCH$_3$ and Si-CH$_3$ contents (mol%) of their terminal groups were analyzed by means of NMR analysis(Bruker Co.). The results are set forth in the following Table 1.

Table 1

Precursor	MW	MWD	Si-OH (%)	Si-OCH$_3$ (%)	Si-CH$_3$ (%)
Precursor (A)	60800	6.14	35.0	1.2	63.8
Precursor (B)	4020	2.77	39.8	0.5	59.7
Precursor (C)	63418	6.13	26.3	0.7	73.0

·Si-OH(mol%)=Area(Si-OH)÷[Area(Si-OH)+Area(Si-OCH$_3$)/3+Area(Si-CH$_3$)/3]×100

·Si-OCH$_3$(mol%) =Area(Si-OCH$_3$)/3÷[Area (Si-OH)+Area(Si-CH$_3$)/3+Area(Si-CH$_3$)/3]×100

·Si-CH$_3$(mol%)   =Area(Si-CH$_3$)/3÷[Area(Si-OH)+Area(Si-OCH$_3$)/3+Area(Si-CH$_3$)/3]×100

Example 4: Determination of thickness and refractive index of the thin film made from the substance having nano-pores

[0048] The resinous compositions of the present invention were prepared by mixing the siloxane-based resinous matrix precursor obtained from the above Example 2 together with saccharide based-porogen and propylene glycol methyl ether acetate (PGMEA) in accordance with the particular ratios as described in the following Table 2. These compositions were applied to spin-coating at 3000rpm onto p-type silicon wafers doped with boron. The substrates thus coated were then subjected to a series of soft baking on a hot plate for 1min at 150°C and another min at 250°C, so that the organic solvent might be sufficiently removed. Then, the substrates were cured in a Linberg furnace at 420°C for 60mins under vacuum condition. Thereafter, the thickness of each resulting low dielectric film was determined by using prism coupler and the refractive index determined by using prism coupler and ellipsometer. The results are set forth in the following Table 2.

Table 2

Example	Matrix precursor	Porogen	Mat. [1] (wt. %)	CD[2] (wt.%)	Thickness (Å)	Dielec tric constant (k)
Example 4-1	Precursor A	Not added	25.0	-	8245	1.437

Table 2   (continued)

Example	Matrix precursor	Porogen	Mat. [1] (wt. %)	CD[2] (wt.%)	Thickness (Å)	Dielec tric constant (k)
Example 4-2	Precursor A	Sucrose octabenzoate	25.0	30	8637	1.328
Example 4-3	Precursor B	Not added	30.0	-	10424	1.414
Example 4-4	Precursor B	Sucrose octabenzoate	30.0	30	11764	1.304
Example 4-5	Precursor C	Not added	25.0	-	11340	1.440
Example 4-6	Precursor C	Glucose pentaacetate	25.0	35	10247	1.418
Example 4-7	Precursor C	Sucrose octaacetate	25.0	35	13942	1.318
Example 4-8	Precursor C	Sucrose octabenzoate	25.0	35	8578	1.298

·Mat.[1] (wt.%) = [weight of matrix precursor (g)+weight of porogen(g)] / [weight of PGMEA(g)+weight of precursor(g) + weight of porogen(g)] x 100

·CD[2] (wt.%) = weight of porogen(g) / [weight of porogen(g)+weight of matrix precursor(g)] x 100

Example 5: Preparing determiner of dielectric constant of the thin film and determination of dielectric constant of the thin film

[0049]   To determine the dielectric constant of the porous thin film , 3000Å thickness silicon thermo oxide film were applied onto p-type silicon wafers doped with boron, then 100Å titanium , 2000Å aluminum were deposited by metal evaporator. Subsequently, low dielectric films in composition of Table 3 were coated as example 4. Thereafter, 1mm diameter circular aluminum thin film is deposited at 2000Å thickness by the hard mask designed to have 1mm electrode diameter to complete [MIM(Metal- insulator-metal)]-dielectric constant determiner in [MIM(Metal-insulator-metal)] structure. Capacitance of these thin films was measured by PRECISION LCR METER(HP4284A) with Probe station (Micromanipulator 6200 probe station), at 100Hz frequency. The thickness of thin film measured by a prism coupler is substituted into following equation, to provide the electric constant.

$$k = (C \times d) / (\varepsilon_0 \times A)$$
k : dielectric constant
C : capacitance
d : the thickness of the low dielectric thin film
ε_0 : dielectric constant in vacuum
A : the contact area of electrode

Table 3

Example	Matrix precursor	Porogen	Mat. (wt . %)	CD (wt.%)	Pore Content[1] (%)	Dielectr icconstant (k)
Example 5-1	Precursor B	Not added	25.0	-	-	2.75
Example 5-2	Precursor B	Sucrose octabenzoate	25.0	10	4.1	2.52
Example 5-3	Precursor B	Sucrose octabenzoate	25.0	20	10.9	2.19
Example 5-4	Precursor B	Sucrose octabenzoate	25.0	30	20.5	2.01
Example 5-5	Precursor C	Not added	25.0	-	-	2.92

Table 3 (continued)

Example	Matrix precursor	Porogen	Mat. (wt . %)	CD (wt.%)	Pore Content[1] (%)	Dielectr icconstant (k)
Example 5-6	Precursor C	Glucose pentaacetate	25.0	35	3.9	2.82
Example 5-7	Precursor C	Sucrose octaacetate	25.0	35	10.7	2.56
Example 5-8	Precursor C	Sucrose octabenzoate	25.0	35	27.0	1.94
Pore Content[1] (%) = calculated from the refraction index measured by using prism coupler, by Lorentz-Lorentz equation						

Example 6: Measuring of the average size and size distribution of the pores in the prepared porous thin film

[0050]   Nitrogen adsorption analysis with Surface Area Analyzer[ASAP2010, Micromeritics co.] was performed to analyze the pore structure of the thin films prepared by the same process as in Example 4 in the composition of following Table 4. Thin film has very small average size less than 20Å as described in Table 4. Fig.1 and Fig 2 describe pore size distributions of the thin film prepared in Examples 6-3 and 6-4.

Table 4

| Example	Matrix precursor	Porogen	Mat. (wt.%)	CD (wt.%)	Average pore size (Å)	Volume of pore (cc/g)	Surface area (m²/g)
Example 6-1	Precursor C	Not added	25.0	-	6.1	0.008	164
Example 6-2	Precursor C	Glucose pentaacetate	25.0	30.0	16.2	0.166	412
Example 6-3	Precursor C	Sucrose octabenzoate	25.0	30.0	14.6	0.451	631
Example 6-4	Precursor C	Sucrose octabenzoate	25.0	30.0	16.3	0.455	681

Claims

1.   A composition for preparing substances having porous interlayer dielectric thin film, said composition comprising:

> a saccharide or saccharide derivative;
> a thermo-stable organic or inorganic matrix precursor; and
> a solvent for dissolving both the saccharide or saccharide derivative and the matrix precursor.

2.   The composition according to claim 1, wherein the content of the saccharide or saccharide derivative is 0.1-95 wt. % of the solid components(the matrix precursor + the saccharide or saccharide derivative).

3.   The composition according to claim 1 or 2, wherein the content of the solvent is 20.0~99.9 wt.% of the compositions (the matrix precursor + the saccharide or saccharide derivative + the solvent).

4.   The composition according to any of claims 1 to 3, wherein the saccharide or saccharide derivative is selected from one or more monomeric saccharide derivatives represented by the following formulae(8) to (10):
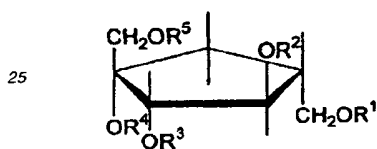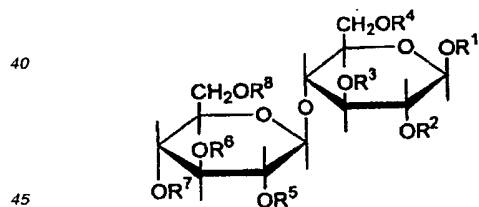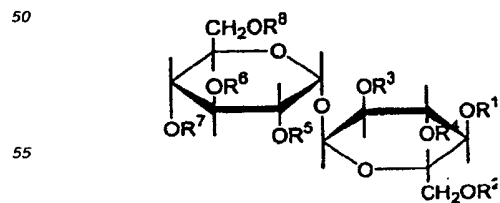
(8)

(9)
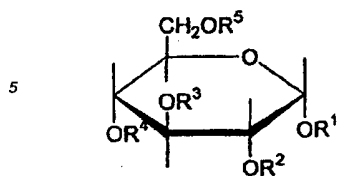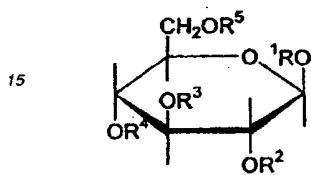
(10)

in which, R_1, R_2, R_3, R_4 and R_5 are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10} cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group, or C_{1-20} carboxyl group.

5. The composition according to any of claims 1 to 3, wherein the saccharide or saccharide derivative is selected from disaccharide derivatives represented by the following formulae (11) to (13):
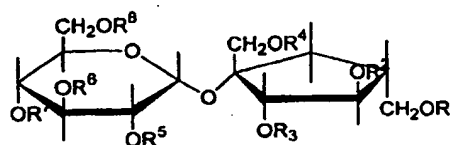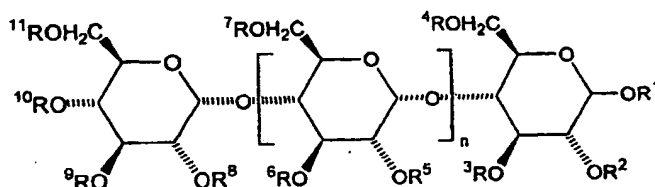

(11)

(12)

$$(13)$$

in which, R_1, R_2, R_3, R_4, R_5, R_6, R_7 and R_8 are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10} cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group, C_{1-20} carboxy alkyl group.

6. The composition according to any one of claims 1 to 3, wherein the saccharide or saccharide derivative is selected from polymeric saccharide derivatives represented by the following formula (14)

$$(14)$$

in which, R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} are independently hydrogen atom, C_{2-30} acyl group, C_{1-20} alkyl group, C_{3-10} cycloalkyl group, C_{6-30} aryl group, C_{1-20} hydroxy alkyl group, or C_{1-20} carboxyl group and n is an integer ranging from 1 to 20.

7. The composition according to any of claims 1 to 3, wherein the saccharide or saccharide derivative is glucose, glucopyranose pentabenzoate, glucose pentaacetate, galactose, galactose pentaacetate, fructose, sucrose, sucrose octabenzoate, sucrose octaacetate, maltose or lactose.

8. The composition according to any of claims 1 to 7, wherein the matrix precursor is silsesquioxane, alkoxysilane sol, or siloxane-based polymer.

9. The composition according to claim 8, wherein the silsesquioxane is hydrogen silsesquioxane, alkyl silsesquioxane, aryl silsesquioxane, or a copolymer thereof.

10. The composition according to claim 9, wherein the matrix precursor is a siloxane-based resin which is prepared by hydrolysis and polycondensation of one or more monomers selected from compounds represented by the following formulae (1) to (4), using a catalyst and water in an organic solvent:
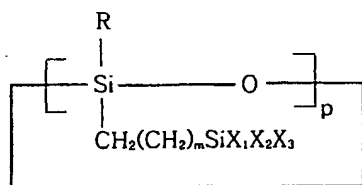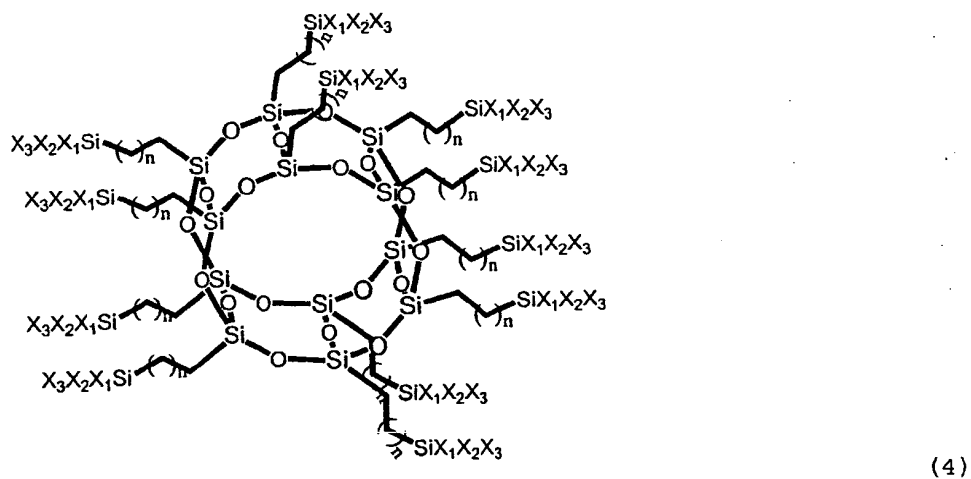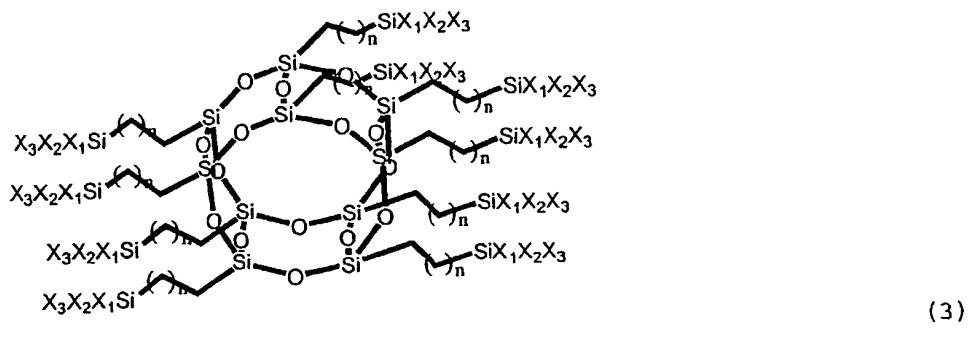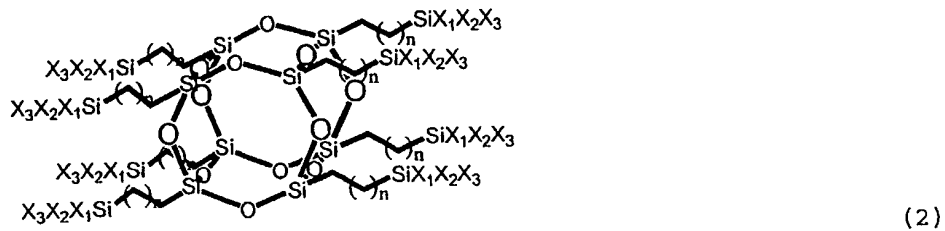

$$(1)$$

in which, R is hydrogen atom, C_{1-3} alkyl group, C_{3-10} cycloalkyl group, or C_{6-15} aryl group;

X_1, X_2 and X_3 are independently C_{1-3}, alkyl group, C_{1-10} alkoxy group, or halogen atom, and at least one of

them is a hydrolysable group;

p is an integer ranging from 3 to 8;

m is an integer ranging from 0 to 10; and

5

(2)

10

15

20

(3)

25

30

35

(4)

40

45

50

55

in which, X_1, X_2 and X_3 are independently C_{1-3} alkyl group, C_{1-10} alkoxy group, or halogen atom, and at least one of them is hydrolysable; and

n is an integer ranging from 1 to 12.

11. The composition according to claim 1, wherein the matrix precursor is siloxane-based resin which is prepared by

hydrolysis and polycondensation of a mixture of one or more monomers selected from compounds represented by the formulae (1) to (4) as defined in claim 10, together with one or more silane-based monomers selected from compounds represented by the following formulae (5) to (7) using a catalyst and water in an organic solvent:

$$SiX_1X_2X_3X_4 \qquad (5)$$

$$RSiX_1X_2X_3 \qquad (6)$$

$$R_1R_2 SiX_1X_2 \qquad (7)$$
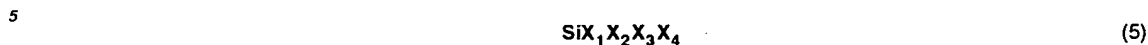
in which, R_1 and R_2 are respectively hydrogen atom, C_{1-3} alkyl group, C_{3-10} cycloalkyl group, or C_{6-15} aryl group; and X_1, X_2, X_3 and X_4 are independently C_{1-3} alkyl group, C_{1-10} alkoxy group, or halogen atom.

12. The composition according to any of claims 1 to 11, wherein the content of the matrix precursor is more than 10 mol%.

13. The composition according to claim 11 or 12, wherein the mole ratio of the siloxane monomers having cyclic or cage structure to the silane-based monomers is 0.99:0.01~0.01:0.99.

14. The composition according to any of claims 1 to 7, wherein the matrix precursor is polyimide, polybenzocyclobutene, polyarylene, or a mixture thereof.

15. The composition according to any of claims 1 to 14, wherein the solvent is aromatic hydrocarbon-based solvent, ketone-based solvent, ether-based solvent, acetate-based solvent, amide-based solvent, γ-butyrolactone, silicon-based solvent, or a mixture thereof.

16. A method for forming dielectric thin films between interconnect layers in semiconductor devices, said method comprising:

coating a composition according to any of claims 1 to 15 on a substrate through spin-coating, dip-coating, spray-coating, flow-coating, or screen-printing;
evaporating the solvent therefrom; and
heating the coating film at 150~600°C under inert gas atmosphere or vacuum condition.

17. The method according to claim 16, wherein the coating is carried out by spin-coating at 1000~5000rpm.

18. A substance having nano-pores, said substance being prepared by using the composition comprising a saccharide or saccharide derivative, a thermo-stable organic or inorganic matrix precursor, and a solvent for dissolving both the saccharide or saccharide derivative and the matrix precursor.
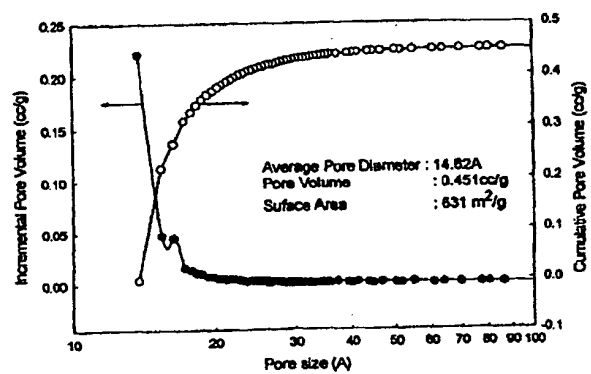
FIG. 1

FIG. 2